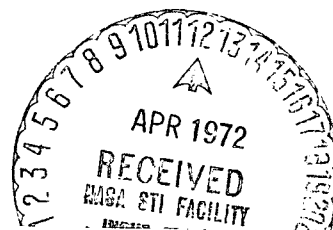


USE OF A LASER FOR ATOMIC ABSORPTION ANALYSIS

E. P. Krivchikova, V. S. Demin

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## USE OF A LASER FOR ATOMIC ABSORPTION ANALYSIS

E. P. Krivchikova, V. S. Demin

ABSTRACT. Localization of a laser beam in a small area of a solid steel sample (steel with high Cr content) is described. A continuous spectrum with absorption lines (due to absorption of atoms mainly) is emitted and registered by a spectrograph. The lines Ni I 2320.0, Cr I 3015.5, Mn I 2794.8, and Si I 2516.1 Å were used to determine 0.1-1% Ni, Mn, and Si and 9-17% Cr in steel. The calibration curves are linear; the mean relative error is 3%.

Optical masers (lasers) are attracting attention because their practical /592\* applications are manifold. References [1-4] used a laser as a source of excitation for emission spectral analysis. These investigations showed that the laser excitation source has many advantages over arc or spark excitation.

Investigation of the spectrum of high chrome steel excited by a laser revealed that many of the analytical lines of analyzed impurities are absorption lines. This paper is devoted to the investigation of the possibility of using a laser beam for atomic absorption spectral analysis. The experiments were conducted using a GOR-100M pulsed laser operating in the free-running mode. Laser radiation was sharply focused on the surface of the specimen by a lens with a focal length  $f = 50$  mm.

The physical processes associated with the destructive action of laser radiation focused on metal are very similar to those that take place in a high-current pulse discharge. The destructive processes in the case of these sources are of heat origin. All the energy is concentrated within a small area of specimen surface and this results in its explosive-like evaporation [5-10]. The numerous investigations of spark discharge now make it obvious that the formation of vapors from the metal of electrodes takes place in the form of luminous streams flying off normal to the surface of the electrodes at a speed reaching several thousands of meters per second [11-15]. The destruction of the

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\* Numbers in the margin indicate pagination in the foreign text.

material by the laser also is accompanied by the formation of plasma streams propagating perpendicular to the surface of the material, and in the case of both sources there is an intermittent plasma emission. The plasma can move at a rate of 20 km/sec [9,10]. Hydrodynamic phenomena play a significant role in plasma stream processes. These phenomena too are characteristic of both sources.

Qualitative investigations of the spectra of plasma streams formed by laser radiation have revealed that they are similar to the spectra of pulse discharges [5, 6, 8, 9, 16].

We investigated the spectra of ruby, alundum, and high chrome steel alloyed with manganese nickel, and silicon. The spectra of the materials investigated, attributable to the effect of a laser beam, are a continuous background, against which are seen the absorption and emission lines. The absorption lines are due primarily to neutral and singly ionized atoms with an excitation energy of 5 to 7 eV (the lines Cr I 2408.6 Å, Ni I 2325.8 Å, Si I 2506.9 Å, Mn I 2794.8 Å in steel; Al I 2660.4 Å, Al I 2575.1 Å, in alundum and ruby; Cr I 3578.7 Å, Cr I 3593.5 Å in ruby; Ti I 2520.5 Å, Ti I 2727.4 Å in alundum, for example). Lines of doubly ionized atoms occurred only in emission. The neutral atom lines were observed to show the most absorption. Absorption of ions by the lines was poorly defined. The absorption lines for the materials investigated can be characterized by a high degree of diffusivity. A shift relative to the emission lines for iron, obtained in an arc source, was observed for some lines. This was equally true of absorption lines and emission lines. Thus, qualitative investigations of the spectra obtained as a result of laser radiation of a substance revealed a great similarity to the spectra in pulse discharges [11-14]..

It is now known that it is possible to use atomic absorption spectra of a powerful pulse discharge in a capillary to solve analytical problems [11]. We have shown that it is possible to use atomic absorption spectra obtained in a laser source for analytical purposes.

We know [17-19] that the magnitude of the total energy,  $A$ , absorbed by the lines of a continuous spectrum in the case of weak absorption equals  $A = \frac{\pi e^2}{mc} l f N$ , where  $m$  is the electron mass,  $e$  is the electron discharge,  $c$  is the speed of light,  $l$  is the length of the absorbing layer,  $f$  is the oscillator strength, and  $N$  is the atom concentration. The magnitude of the total absorption for low

optical densities is proportional to the magnitude  $1fN$  (the linear section of the "growth curve"), and for high to the  $\sqrt{1fN}$ . Total absorption in the line is measured by the area contained between the contour of the absorption line and the continuous background [17-19].

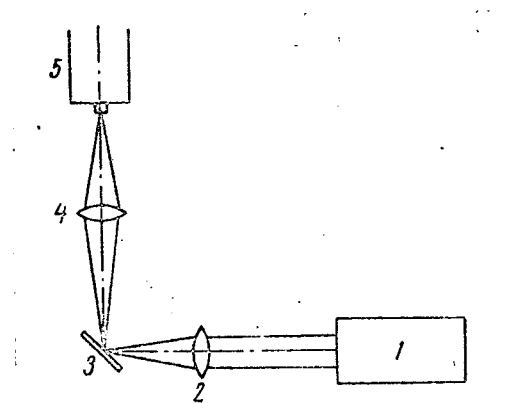


Figure 1. Optical schematic of the laser installation.  
1 - laser; 2 - lens,  $f = 50$  mm; 3 - specimen; 4 - lens,  $f = 75$  mm; 5 - ISP-22 spectrograph.

We used the total absorption method and laser evaporation of a specimen to analyze high chrome steel for impurities. Manganese, nickel, and silicon were determined as being in the concentration interval between 0.1 and 1 percent, and chromium in the interval between 9 and 17 percent. The optical schematic of the installation is shown in Figure 1. The specimens were positioned at an angle of  $45^\circ$  to the axis of the laser beam and the optical axis of the spectrograph. The spectra were photographed under identical conditions using  $7 \cdot 10^6 \text{ W/cm}^2$  of light energy. The laser beam was focused to a point on the surface of the specimen. The quantity of material ejected by the radiation injury was the same for all specimens,  $\sim 3.5$  mg. An ISP-28 spectrograph was used to register the spectra. Single lens illumination of the spectrograph slit ( $f = 75$  mm) was used. One flash was sufficient to obtain normal blackening of a continuous spectrum on RF-3 photographic film with a sensitivity of 650 units GOST.

The lines Ni I 2320.0 Å, Cr I 3015.2 Å, Mn I 2794.8 Å, Si I 2516.1 Å were selected for atomic absorption spectrum analysis. The contours of the line were constructed for each element contained in the steel, and the ratio between the total absorption in the line,  $A$ , and the content,  $C$ , of the element in the

specimen was calculated. Figure 2 shows the curves, and the fact that the points fall along a straight line. The root-mean-square error of the determination is about 5 percent. The contours of the lines were registered by a microphotometer. The register was based on the EPP-09 recording potentiometer. A planimeter was used to find the areas of the contours. The advantage of this method is that the magnitude of the total absorption is independent of the resolution of the spectrum instrument over considerable limits [17-19].

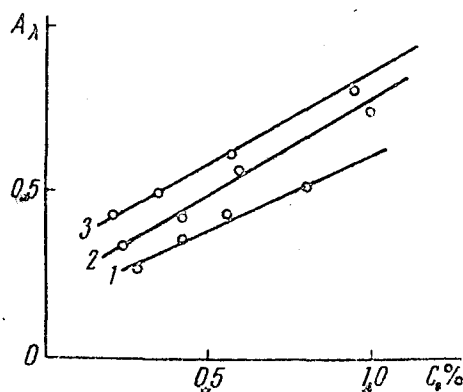


Figure 2. Calibration curves for determination of nickel (1), manganese (2), and silicon (3) in steel by the total absorption method.

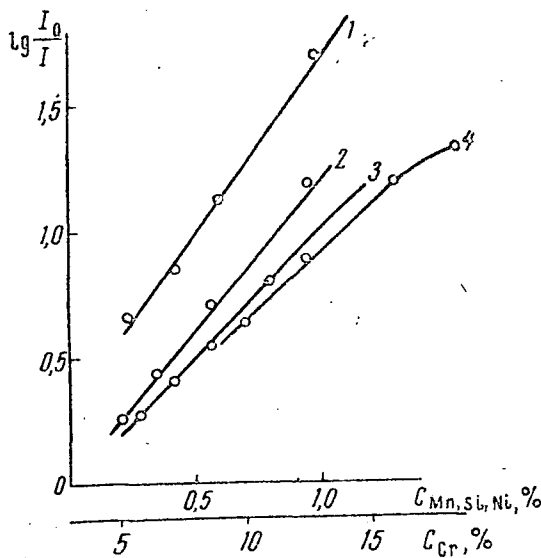


Figure 3. Calibration curves for determining manganese (1), silicon (2), nickel (3), and chromium (4) in terms of optical density measurement.

Yet another measurement scheme was used to determine the impurities in high chrome steel. We can, knowing the concentration of an element in the specimen, and measuring the optical density of the line [20,21], construct curves in  $\log I_0/I$  coordinates. Resolution must be good in order to obtain a high degree of sensitivity in this case. Figure 3 shows the calibration curves for this relationship. The optical density increases linearly within the limits shown in the figure for the concentrations of elements. The points for the experimental data fall along a straight line quite satisfactorily. The linearity does not hold for heavy concentrations, however (the maximum is different for each element). In the case of chromium, for example, its deviation from the linear relationship is seen when its content is above 18.5 percent. The root-mean-square error in the determination by this method is approximately 4 percent. The table lists the mean values of concentrations of nickel, chromium, manganese, and silicon obtained from three determinations made during the laser excitation of steel (the concentrations of nickel, chromium, manganese, and silicon were found from the curves for optical density in terms of concentration). The reproducibility of the results was verified by photographing the same specimen 595 twenty times. The root-mean-square error in the reproducibility of the results is about 3 percent.

RESULTS OF THE ANALYSIS OBTAINED IN A LASER SOURCE

Elements	Interpolated percent by weight	Found in laser, per- cent by weight
Silicon	0.35	0.37
Nickel	0.42	0.41
Manganese	0.42	0.42
Chromium	16	16.5

The optical density of the spectral for the impurities in terms of lasing flux density was investigated in order to select the optimum conditions for analyzing high chrome steel for impurities. The optical density of the spectral lines increased in proportion to the energy with change in the laser energy density from  $5.7 \cdot 10^6$  to  $1 \cdot 10^7$  W/cm<sup>2</sup>. So it is seen that in order to increase

sensitivity when analyzing small concentrations of an element in a specimen it is necessary to increase lasing energy density and to decrease it when determining high concentrations.

What should be taken into consideration when selecting the analytical lines is that the optical density increases with increase of oscillator strength. The calculation for three manganese resonance lines, Mn I 2801.1 Å, Mn I 2798.2 Å, Mn I 2794.8 Å, showed that an increase in oscillator strength by factors of 1.38, 1.45, and 2, increased the optical density by factors of 1.65, 1.76, and 2.92, respectively.

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